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SHORT COMMUNICATION

Biosorption of Cu^{+2} by Green Algae, *Ulva fasciata*: Optimization by Response Surface Methodology

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Abstract

U. fasciata biomass, a green algae was used as adsorbent, investigated and optimized the environmental parameters using central factorial design for the Cu^{+2} removal. Biosorption of Cu^{+2} involves the functional groups –CO, –OH, and N–H of *U. fasciata* biomass. Various parameters were estimated using Response Surface Methodology (RSM), including pH (4–6), initial Cu^{+2} concentration (60–140 mg L^{-1}), biomass dosage (0.08–0.40 g L^{-1}) and temperature (20–40 °C). It was found that the uptake of Cu^{+2} by *U. fasciata was* 62.31 mg L^{-1} at an initial concentration of 80 mg L^{-1}, a temperature of 35 °C, and a pH of 5.245. In order to analyze the equilibrium data, applied Langmuir, Freundlich, Langmuir-Friendly (L-R), and Redlich-Peterson (L-R) isotherm models. The multiple mechanisms were involved in the removal of Cu^{+2} including chelation, ion-exchange and adsorption on *UF* biomass. It is believed that the *U. fasciata* biomass is a suitable material for the removal of Cu^{+2} ions from wastewaters.

Keywords *Ulva fasciata* · Response surface methodology · FT-IR · SEM · X-Ray diffraction

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Significance Statement

U. fasciata (*UF*) an algae biomass abundantly available in the oceans. Cu^{+2} is toxic (1.3 mg L^{-1}) accumulated in ecosystems, causing adverse effects to humans. In this work, Cu^{+2} is removed from solutions and parameters were optimized by RSM. The biomass was characterized by X-RD, SEM and FTIR.

Heavy metals like Cu^{+2} are among the most toxic to living organisms [1] and exposure can cause anemia, gastrointestinal distress, and kidney damage in humans [2]. The Environmental Protection Agency (EPA) recommends less than 1.3 mg L^{-1} of Cu^{+2} in potable water. In addition to removing Cu^{+2} from potable water [3], biosorption uses quiescent and decomposing biomass to remove metal ions [4]. Algae is a renewable natural biomass that proliferates widely [5], abundantly, and can adsorb heavy metals [5]. Research has shown that marine algae can adsorb heavy metal ions [6, 7] and few studies have investigated the uptake of Cu^{+2} by *Ulva fasciata* (*UF*) biomass. Response surface methodology (RSM) [6] analyzes multiple regressions of quantitative data that result in higher yields with lower biosorption costs. It is possible to analyze the interactions of the test variables and their effects on the response using a response surface [8, 9]. Hence, this study examined the feasibility of using *UF* biomass to remove Cu^{+2} from aqueous solutions through RSM [10]. Variables that affect biosorption (pH, contact time, biomass dosage, and temperature) were optimized.

Ulva fasciata, a green alga was obtained from Bay of coast, Visakhapatnam, Andhra Pradesh, India. The biosorbent algae, *UF* was prepared according to our previous work Sarada et al., (2014) [7] and characterization conditions were briefly explained in text S1. Further the design of central composite design (CCD) was also explained in text S2. The results of SEM (fig. S1), XRD (fig. S2) and FTIR (Fig. 1) results were described in text S3. Figure 1 shows the involvement of functional groups present on *UF* biomass are –CO, –OH, and N–H in the removal of Cu^{+2}. The effect of time was discussed in text S3 (fig. S3a).

Polynomial quadratic equations were the most suitable fit and the correlation coefficient (R^2), the statistical model can explain 96.53% of the variation. In Figure S3(b), the predicted and detected values are correlated. The diagonal line connects all points, indicating a strong correlation between detected and predicted values. A modified calculation of R^2 allows for a sample size and the number of model parameters. The improved correlation coefficient (Adj $R^2 = 0.9330$) confirms the model's high significance [11]. In this case, the modified R^2 coefficient is 0.9330, lower than the R^2 value of 0.9653. Based on the adjusted R^2 of 0.9330, the predicted R^2 of 0.8510 is reasonable. It indicates superior experiment precision and reliability when the coefficient of variation is relatively low (CV = 2.86%) [8, 11, 12]. Based on response surface methodology, Cu^{+2} removal and the test variables in coded units (Eq. 1) were empirically related.

$$\begin{aligned} Y &= 70.5496 + 2.8828X_1 - 0.3983X_2 - 3.3260X_3 + 1.8205X_4 \\ &- 4.4102X_1^2 - 2.6400X_2^2 - 1.6121X_3^2 - 1.5509X_4^2 \\ &- 0.1679X_1X_2 + 0.1094X_1X_3 - 0.0632X_1X_4 \\ &- 0.8259X_2X_3 + 2.2236X_2X_4 - 1.0394X_3X_4 \end{aligned} \quad (1)$$

where X_1, Biomass loading (mg); X_2, pH; X_3, Initial metal concentration (mg L^{-1}); X_4, Temperature (°C). X_1^2, X_2^2, X_3^2, X_4^2 = Square effects. $X_1 \times X_2$, $X_1 \times X_3$, $X_1 \times X_4$, $X_2 \times X_3$, $X_2 \times X_4$, $X_3 \times X_4$, = Interaction effects.

The greater the t-value and the smaller the P-value [8], the greater the significance. Figure 2 shows the regression model as 2D and 3D surface and contour plots. Contours in Fig. 2a–2c are circular, so biomass does not interact with other variables (Fig. 2d to 2f explained in supplementary file text S4). Moreover, table S1 shows that biomass weights between 0.25–0.28 g 50 mL^{-1} are optimal for efficient Cu^{+2} removal. The significant results were obtained by RSM: 0.264 g of biomass 50 mL^{-1}, pH 5.24, initial Cu^{+2} of 80 mg L^{-1} and at 35°C by converting the encoded values to their natural values. The isotherm models (Freundlich, Langmuir, Langmuir-Freundlich and Redlich–Peterson) used for the experimental data are given in text S4. The linear plots of log q_e versus log C_e (Fig. 3a) demonstrate that the Freundlich model adequately represented the data at various Cu^{2+} levels and pH values. Freundlich constant value (1.4010 and 2.2578) across 1 and 10 implies a more favorable trend (Table 1). Ce/qe versus Ce generated a straight line (Fig. 3b) via R^2 of 0.9977, suggesting that the adsorption results could be described by Langmuir equation. Affinity constant 'b' values of 0.0119 and 0.0194 mg L^{-1} suggest (Table 1) the fact that the adsorption ability of *UF* for Cu^{2+} is more substantial and favoured. The same pattern has been found for the removal of Pb^{+2} on algae *C. fastigiata* and on *Jania rubens* [7, 13]. At small amounts, it drops to the Freundlich isotherm, violating Henry's law. It predicts Langmuir isotherm monolayer sorption capacity at high contaminant levels. K_{LF}, a_{LF}, and n are for pH 5 found 0.00029, 18.6915, and 1.906 having R^2 value 0.999 (Table 1). The similar results were observed in previous work on *A. heterophylla*, a plant biomass for removal of Cd^{+2} [14]. According to reports, the Redlich–Peterson isotherm equation [15] accurately described Fe^{3+} biosorption by *Synechocystis* sp. PCC 6803. To determine the K_{rp} and α_{rp} values, a nonlinear regression examination was performed using sigma plot 8.0 and given in Table 1.

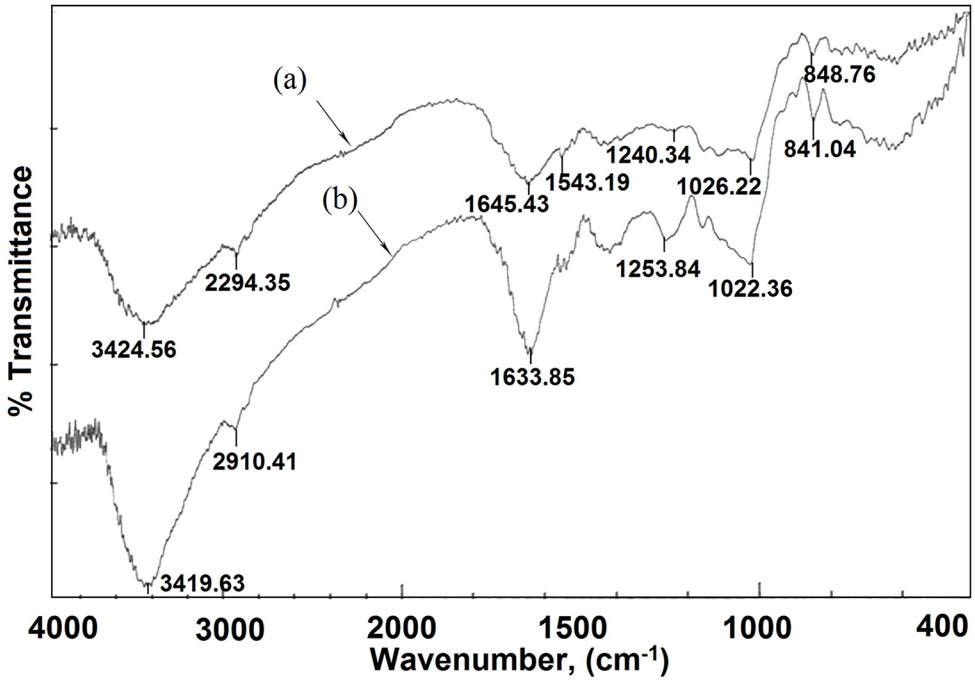

Fig. 1 FTIR spectra of *U. fasciata* **(a)** before adsorption, **(b)** after adsorption of Cu^{+2}

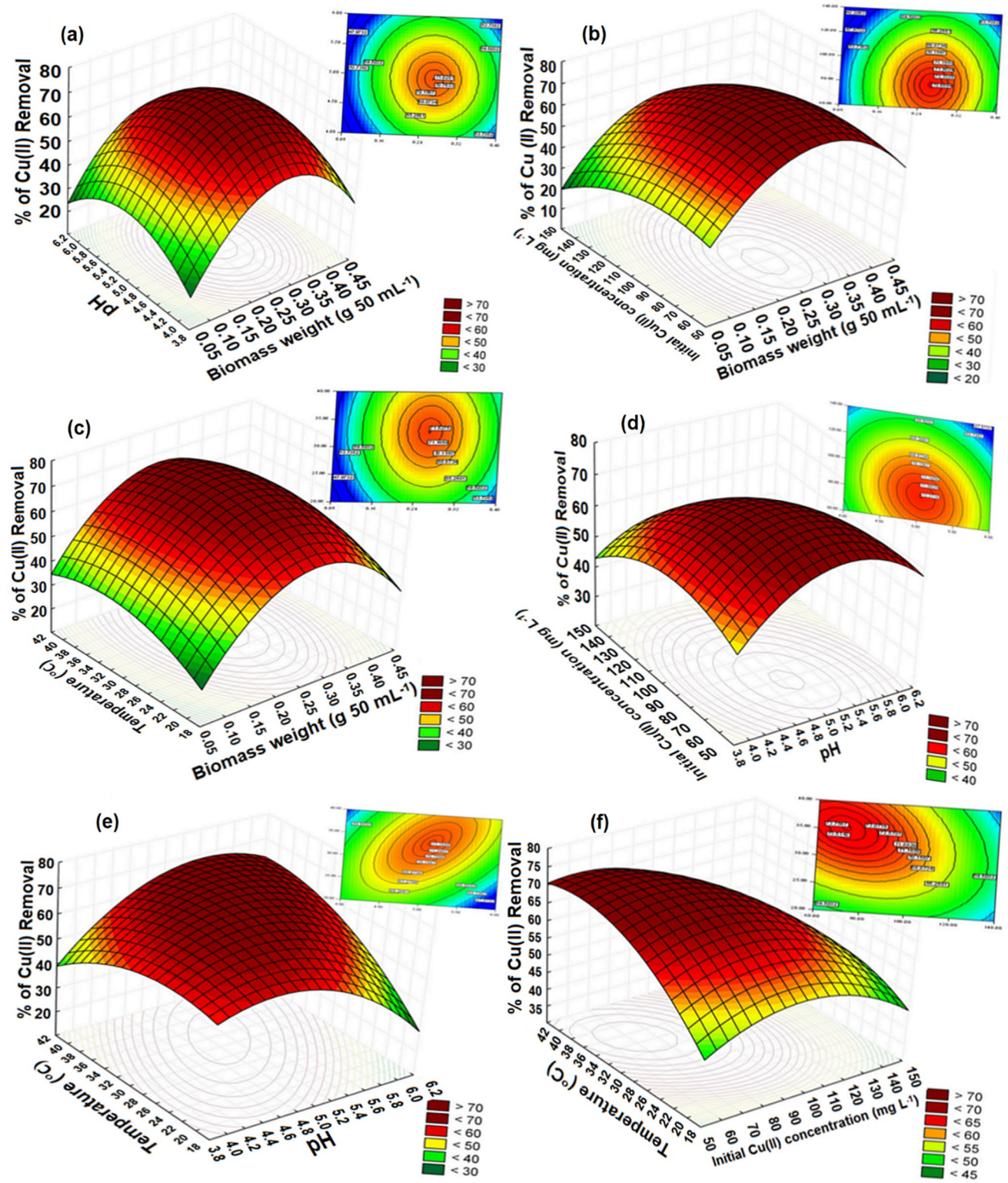

Fig. 2 Surface & Contour plots of Cu^{+2} adsorption removal efficiency (%): **(a)** Biomass weight Vs pH; **(b)** Biomass weight Vs initial metal concentration; **(c)** Biomass weight Vs Temperature; **(d)** pH Vs initial metal concentration **(e)**; pH Vs Temperature; **(f)** Initial metal concentration Vs Temperature

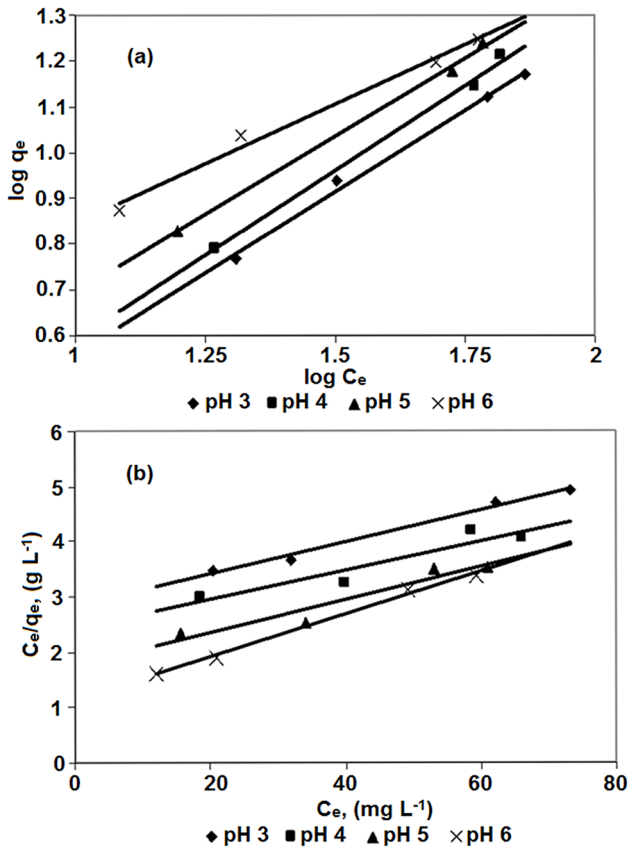

Fig. 3 **(a)** FreundlichIsotherm **(b)** Langmuir isotherm of Cu^{+2} biosorption on *U. fasciata*

Table 1 The constants obtained from the isotherm models at different initial pH values

Isotherm	parameter	pH 3	pH 4	pH 5	pH 6
Experimental	q_{max} (mg g^{-1})				29.71
Freundlich	n	0.692	0.6897	0.6093	0.5021
	K_f(mg g^{-1})	0.7617	0.8882	1.4070	2.2578
	R^2	0.9996	0.9971	0.9960	0.9993
Langmuir	q_{max}(mg g^{-1})	33.8222	35.818	31.307	25.836
	b (mg L^{-1})	0.01054	0.01196	0.01944	0.03409
	R^2	0.9998	0.9977	0.9973	0.9996
Langmuir–Freundlich	a_{LF}	23.364	-0.0067	18.6915	22.9357
	K_{LF}	0.00075	0.99885	0.00029	0.02814
	n	1.2579	0.00020	1.906	1.141
	R^2	0.9999	0.8822	0.9994	0.9998
Redlich–Petersen	β	1.2837	1.6922	1.8051	0.8746
	K_{rp} (L g^{-1})	0.00250	0.000042	0.00042	0.06915
	α_{rp} ((Lmg^{-1}) β)	129.870	8333.33	1111.11	14.6412
	R^2	0.998	0.998	0.9979	0.9997

Based on present study applying 2 level 4 factor (2^4) full factorial CCD, the optimal conditions i.e. initial Cu^{2+} level, pH, temperature and *UF* weight were 80 mg L^{-1}, 5.245, 35 °C and 5.28 g L^{-1} respectively. *UF* biomass was found to have an optimal adsorption ability of Cu^{2+} as 35.81 mg Cu^{2+} g *UF* biomass^{-1}. The FTIR analysis showed that the primary functional groups involved are –CO, –OH and N–H peaks 3437.46, 1240.34 and 849.76 cm^{-1} were shifted to 3441.32, 1253.84 and 841.04 cm^{-1} indicated that involved in the biosorption of Cu^{2+}. Further the morphology was changed in SEM from amorphous crystalline, the X-RD peaks were changed to deformed hexagonal crystalline structure after adsorption of Cu^{2+}. This indicated that the multiple mechanisms were involved such as chelation, ion-exchange and adsorption of Cu^{2+} ions on *UF* biomass.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s40009-024-01419-y.

Author Contributions KKK and KPM designed and initialized the concept in whole experiment. SS and KKK performed the tests and experiments, TS is designed the RSM and optimization studies and KKK written the first draft of the paper. KPM revised the draft of the manuscript.

Declarations

Ethical Approval Not applicable.

Informed Consent Not applicable.

Conflict of Interest The authors declare that there is no financial or any other conflict of interest.

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